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(54) Title: WATER RESISTANT, REMOVABLE ACRYLIC EMULSION PRESSURE SENSITIVE ADHESIVE (57) Abstract A water-resistant, removable pressure sensitive adhesive for use with transparent film facestocks comprises an acrylic-based emulsion polymer composition comprising 85 to 97 % by weight alkyl acrylate monomers, up to 3 % by weight polar monomers, up to 1 % by weight internal crosslinking agent and up to 2 % by weight external crosslinking agent.		

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WATER RESISTANT, REMOVABLE ACRYLIC
EMULSION PRESSURE SENSITIVE ADHESIVE

Field of the Invention

15 This invention relates to removable pressure-sensitive adhesives and more particularly to water resistant, removable acrylic emulsion pressure-sensitive adhesives for use with plasticized polyvinyl chloride and other film facestocks.

20

Background of the Invention

Removable pressure-sensitive adhesives are used on a variety of products including labels, tapes, films, and the like, to enable the product to adhere to a substrate and then to later be removed from the substrate without difficulty and without leaving a stain or residue. Currently, commercially available acrylic emulsion removable pressure-sensitive adhesives cannot be used with film facestocks such as plasticized polyvinyl chloride (PVC) which are used in outdoor applications. Such outdoor applications include decorative decals which are applied to substrates such as glass. The typical technique for applying such a decorative decal to a substrate is to spray water on the adhesive and/or substrate so that the decal is slidingly movable over the substrate for ease of positioning. Unfortunately, in such a technique, the acrylic emulsion adhesive film turns milky in contact

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1 with water. For transparent filmstocks, this results
in an undesirable appearance.

For a successful acrylic emulsion removable
pressure-sensitive adhesive to be used with decorative
5 films and decals in outdoor applications, the adhesive
should exhibit good water resistance along with good
anchorage of the adhesive to the film facestock to
assure clean removability from the substrate. The only
current commercially available acrylic emulsion
10 pressure-sensitive adhesives which demonstrate good
water resistance are permanent adhesives, i.e. those
that leave an adhesive residue on the substrate if the
facestock is removed. Currently available removable
acrylic emulsion pressure-sensitive adhesives which
15 demonstrate good anchorage to the film also exhibit
poor water resistance. Accordingly, there is a need
for a removable acrylic emulsion pressure-sensitive
adhesive which combines both good water resistance and
good anchorage to the film facestock.

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Summary of the Invention

The present invention provides a removable acrylic
emulsion pressure-sensitive adhesive which demonstrates
good water resistance and good anchorage to the
facestock. The adhesives of the present invention are
25 particularly adapted for use on plastic film
facestocks, particularly PVC.

The pressure-sensitive adhesives comprise acrylic
emulsion polymers including from about 85 to about 97%
30 by weight alkyl acrylate monomers having from 1 to
about 12 and preferably from about 4 to about 8 carbon
atoms in the alkyl chain. Up to 15% by weight of the
alkyl acrylate monomers can be replaced by vinyl
acetate or other "hard" monomers, i.e., monomers having
35 a glass transition temperature (T_g) of at least 5°C.

The polymers further comprise a positive amount of
up to about 3% by weight of a polar monomer, preferably

1 methacrylic and/or acrylic acid. The polymers further
comprise an internal crosslinking agent, preferably, a
multifunctional acrylate monomer or diallyl maleate, in
an amount of up to about 1% by weight.

5 The polymers also comprise an external crosslinking
agent, preferably a metal salt, more preferably a metal
ammonium carbonate or acetate in an amount of up to
about 2% by weight. Zirconium ammonium carbonate is
presently preferred.

10 The polymers are preferably synthesized in the
presence of a surfactant in an amount of no more than
about 2% by weight.

The invention further comprises a method for
preparing a water resistant removable acrylic emulsion
15 pressure-sensitive adhesive. In the process, an
aqueous pre-emulsion feed is prepared comprising the
acrylic acrylate monomers, polar monomers, internal
crosslinking agent and surfactant. The pre-emulsion
feed is combined with a free radical generating feed
20 preferably a redox emulsion polymerization catalyst.
The preferred redox catalyst comprises a feed
containing a peroxide or hydroperoxide initiator and a
separate feed comprising a reductant e.g. ascorbic
acid, for activating the initiator. After the
25 polymerization reaction has reached completion and the
reaction mixture cooled, the external crosslinker is
added.

The resulting pressure-sensitive adhesive is then
applied to film facestocks to provide a removable
30 pressure-sensitive adhesive which demonstrates good
water resistance.

Detailed Description of the Invention

In accordance with the present invention, there is
35 provided a water resistant, removable pressure-
sensitive adhesive (PSA) composition comprising acrylic
based emulsion polymers particularly useful with film

1 facestocks such as transparent plasticized PVC,
polyurethane, polyester, polyolefin. The removable PSA
composition, when coated onto such a film facestock,
exhibits low peel adhesion, preferably on the order of
5 about 50 to about 300 N/m on stainless steel.

 The acrylic based emulsion polymers comprise from
about 85 to about 97% by weight acrylic acrylate
monomers. Amounts of alkyl acrylate monomers below 85%
are not presently preferred because the resultant glass
10 transition temperature of the adhesive tends to be too
high and the adhesive loses tack. Polymers having more
than about 97% alkyl acrylate monomers are not
preferred because the polymers tend to exhibit
insufficient cohesive strength and leave stains or
15 residue when peeled away from substrates. An amount of
from about 90% to about 97% by weight alkyl acrylate
monomers is presently preferred.

 The alkyl acrylate monomers preferably have from 1
to about 12 carbon atoms in the alkyl chain and more
20 preferably most of the alkyl acrylate monomers comprise
from about 4 to about 8 carbon atoms in the alkyl
chain. The lower alkyl acrylates, i.e. those having 1
to 3 carbon atoms in the alkyl chain, are not preferred
as they tend to effect adhesion properties of the PSA
25 composition, i.e., impart too low of an adhesion, on at
least some substrates. Homopolymers of alkyl acrylates
having more than 12 carbon atoms in the alkyl chain,
tend to be crystalline and are not preferred. However,
non-crystalline co-polymers including alkyl acrylates
30 having more than 12 carbon atoms in the alkyl chain may
be used as desired. Diesters of alpha, beta
unsaturated dicarboxylic acids may also be beneficially
used.

 Polymers with at least the majority of the alkyl
35 acrylate monomers having from about 4 to about 8 carbon
atoms in the alkyl chain are presently preferred as
providing the optimum balance of hardness, adhesion and

1 removability. Exemplary preferred alkyl acrylates
suitable for use in the present invention include 2-
ethylhexyl acrylate, butyl acrylate, heptyl acrylate,
octyl acrylate, isooctyl acrylate, and isobutyl
5 acrylate. Butyl acrylate and 2-ethylhexyl acrylate are
presently preferred.

Up to about 15% of the alkyl acrylate monomer may be
replaced by a hard monomer. Preferred hard monomers
include vinyl acetate, styrene, methyl methacrylate and
10 vinyl pyrrolidone.

The polymer composition comprises up to about 3% of
a polar monomer or blends of polar monomers to impart
mechanical stability and cohesive strength to the
polymer. The term "polar" monomer is meant to include
15 organic acids, amides and alcohols. Examples of polar
monomers include methacrylic acid, acrylic acid,
itaconic acid, maleic acid, acrylamide, methacrylamide,
2-hydroxy ethyl acrylate and the like. Amounts of
polar monomers greater than about 3% are not preferred
20 because such amounts tends to impart too much adhesion
to the adhesive which renders the product non-
removable.

The polymer composition further comprises up to
about 1% by weight of an internal cross-linking agent.
25 The term "internal crosslinking agent" is meant to
include polyfunctional compounds having at least two
non-conjugated carbon-carbon double bonds per molecule
which agent becomes part of the polymer during
polymerization. It has been found that the amount of
30 internal crosslinking agents should not exceed about
1%, as amounts greater than 1% tends to reduce
stability of the acrylate-based emulsion from which the
polymers are prepared. This results in coagulation of
the emulsion particles during preparation. An amount
35 of the internal crosslinking agent above about 0.3% are
not preferred as no additional benefit is typically
observed. Examples of suitable internal crosslinking

1 agents include diallyl maleate, diallyl phthalate and
multifunctional acrylates and methacrylates including
polyethylene glycol diacrylate, hexanediol diacrylate,
ethoxylated trimethylolpropane triacrylate,
5 pentaerythritol triacrylate, propylene glycol
diacrylate and trimethylolpropane trimethacrylate.
Diallyl maleate is presently preferred.

An initiator is used to induce polymerization of the
monomers. Any suitable initiator may be used.
10 Preferred initiators include peroxides and
hydroperoxides. The initiator is presently present in
an amount of about 0.05 to about 0.3% by weight of the
monomers. The presently preferred initiator is a redox
system comprising an organic or inorganic peroxide as
15 the oxidant and suitable reducing agent. Hydrogen
peroxide is the preferred oxidant used in combination
with ascorbic acid or sodium formaldehyde sulfonate as
the reductant. Oxidant to reductant weight ratio is
preferably about 0.5 to 3. Such combinations are
20 preferred as they tend to provide optimum control of
the rate of initiation and of the percentage
conversion, i.e. the amount of polymer formed at any
given time.

The polymer composition further comprises an
25 external cross-linking agent which causes post
polymerization crosslinking in an amount up to about 2%
by weight, and preferably from about 0.1 to about 0.7%
by weight. External cross-linking agents include metal
salts such as zirconium ammonium carbonate, zinc
30 ammonium carbonate, aluminum acetate, zinc acetate and
chromium acetate. The presently preferred external
crosslinking agent is zirconium ammonium carbonate.
Amounts of external crosslinking agent greater than
about 2% are not presently preferred because of
35 undesirable loss of adhesion.

The monomers are preferably polymerized in the
presence of a surfactant or a mixture of surfactants.

1 The total amount of surfactant is preferably below
about 2% by weight of the polymers. Preferred
surfactants include Disponil FES 77, a sodium alkyl
ether sulfate surfactant marketed by Henkel, Aerosol OT
5 75, a sodium dioctyl sulfosuccinate, a surfactant
marketed by American Cyanamide, and Triton X-100 an
octylphenoxypolyethoxy- ethanol marketed by Rohm and
Haas and surfactants which are copolymerizable such as
a sodium salt of styrene sulfonate, sodium vinyl
10 sulfonate manufactured by E. Hoechst, sodium alkylether
sulfonate manufactured by Alcolace, sodium 2-
methacryloyloxyethyl sulfonate manufactured by Dow and
the like. A sodium salt of styrene sulfonate is the
preferred copolymerizable surfactant.

15 A method for preparing acrylic-based emulsion
polymers of the present invention comprises first
preparing a free radical generating feed preferably a
redox emulsion polymerization catalyst comprising an
oxidizer feed and a reductant feed and a pre-emulsion
20 feed. The oxidizer feed comprises water and oxidant,
e.g. hydrogen peroxide or tertiary butylhydroperoxide.
The reductant feed comprises water and a reductant such
as ascorbic acid or sodium formaldehyde sulfoxylate.
The pre-emulsion feed comprises the alkyl acrylate
25 monomers, polar monomers, internal crosslinking agents,
surfactants and water. The initiator and pre-emulsion
feeds can be combined if desired.

30 In the preferred method, the initiator, catalyst and
pre-emulsion feeds are added simultaneously to a
suitable reactor and polymerization occurs.

35 After the polymerization reaction mixture has
cooled, e.g. to 30 to 50°C, an aqueous solution
containing the external crosslinking agent is added to
the composition. It is preferred that a 20% aqueous
solution of the crosslinking agent be used.

 The removable pressure sensitive adhesives of the
present invention provide certain unique advantages.

1 For example, because of their water resistance, they
are particularly useful with clear plastic film
facestocks where either the adhesive or the substrate
is wetted with water before application. In such
5 applications, it is not important if there is an
increase in peel adhesion over time and/or temperature
- only that the adhesive be cleanly removable. In
fact, an increase in peel adhesion alone with clean
removability is generally desirable. Further, the
10 adhesives are based on water-based emulsion technology
rather than more toxic solvent-based technology.

Examples 1-3

15 Examples 1-3, shown in Table 1 below, are
commercially available pressure sensitive products.
Example 1 is a commercially available removable
pressure sensitive adhesive marketed by Avery Dennison
Corp. marketed under the trade designation AE2605.
This pressure sensitive adhesive was prepared according
20 to Example 1 in U.S. Patent No. 4,975,908, which is
incorporated herein by reference. Example 2 is the
same as Example 1 except that 0.5% of zirconium
ammonium carbonate was added as an external crosslinker
after initial polymerization was completed. Example 3
25 is a commercially removable pressure sensitive adhesive
marketed by Avery Dennison Corporation under the trade
designation UVR-150.

Example 4

30 To a four liter, four necked jacketed reactor
equipped with thermocouple, reflux condenser, stainless
steel blade stirrer and nitrogen inlet tube, were
charged 468.75 grams of deionized water, 0.125 g of
NaFeEDTA, 1.0g ascorbic acid, and 0.6g of Disponil FES
35 77, a surfactant sold by Henkel. A monomer mix
consisting of 1245g of butyl acrylate, 232.5g of 2-
ethylhexyl acrylate, 30.75g of methacrylic acid, and

1 33.5g of acrylic acid was added to 190g of water
containing 40g of Disponil FES 77, 1.03g of sodium
bicarbonate, and 5.8g of Aerosol OT 75, a surfactant
5 sold by American Cyanamid and was agitated for
sufficient time until the formation of a stable pre-
emulsion feed. An initiator feed containing 4.35g
hydrogen peroxide in 130g water was prepared. A
reductant feed containing 2.5g ascorbic acid in 130g
10 water was prepared. The contents of the flask were
agitated while purging nitrogen for 15-20 minutes and
then heated to 45C. At 45°C a solution of the
initiator containing 1.7g hydrogen peroxide in 43.2g
water was added. Then the pre-emulsion feed, and the
15 initiator feed, and the catalyst feed were started
simultaneously. The pre-emulsion feed started at a
rate of 6.87 g/min for 30 minutes, then increased the
rate to 8.86g/min for a overall 3.5 hour feed period.
The initiator and catalyst feeds maintained a 0.56
20 g/min rate over a 4 hour period. After all the feeds
had been added, the mixture was tested for the presence
of free monomer. Based on the test results, a second
initiator solution was prepared by adding 0.23g tert-
butyl hydroperoxide (80%), 0.063 ascorbic acid, 0.015g
Disponil FES 77 to 5.94g water and added to the
25 reaction mixture. After 30 minutes another second
initiator solution was added. After 1 hour, the
composition was cooled and neutralized with ammonia,
then filtered through a 300 mesh nylon sieve. The
resulting composition had a solids content of 58%, a
30 percent coagulum of less than 0.01%, and a viscosity of
about 250 centipoise as measured by a Brookfield
viscometer, and a pH of 6.6.

Example 5

35 Example No. 4 was repeated with the exception that
the pre-emulsion mix contained 1345.25g butyl acrylate,
155g vinyl acetate, 15.5g methacrylic acid, 15.5

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1 acrylic acid, 0.8g diallyl maleate, and 8g sodium p-
styrenesulfonate (a copolymerizable surfactant sold by
Toyo Soda Manufacturing Co.).

5 Example 6

Example No. 5 was repeated except that 0.7% by
weight based on the weight of the polymers of zirconium
ammonium carbonate (sold by Magnesium Elektron)
external crosslinker was added to the polymer
10 composition after initial polymerization was completed
and the polymer composition had cooled to about 30°C.

Example 7

Example No. 4 was repeated with the exception that
15 the pre-emulsion mix contained 1260.38g butyl acrylate,
232.5g 2-ethylhexyl acrylate, 23.13g methacrylic acid,
23.13g acrylic acid, and 0.52g diallyl maleate.
Further, 0.5% by weight zirconium ammonium carbonate
was added to the polymer composition after initial
20 polymerization was completed and the polymer
composition had cooled to about 30°C.

Example 8

Example No. 7 was repeated with the exception that
25 the pre-emulsion mix contained 15.5g methacrylic acid,
15.5g acrylic acid, and 15.45g sodium p-
styrenesulfonate. 0.7% by weight zirconium ammonium
carbonate was used.

30 Example 9

Example No. 8 was repeated with the exception that
the pre-emulsion mix contained 7.72g sodium p-
styrenesulfonate.

35 Example 10

Example No. 8 was repeated with the exception that
the pre-emulsion mix contained 5.1g sodium p-

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1 styrenesulfonate. 0.5% by weight zirconium ammonium
carbonate was used.

Example 11

5 Example No. 10 was repeated with the exception that
the pre-emulsion mix contained 0.54g 1,6-hexanediol
diacrylate instead of diallyl maleate.

Example 12

10 Example No. 10 was repeated with the exception that
the pre-emulsion mix contained no diallyl maleate.

Example 13

15 Example No. 10 was repeated with the exception that
1.4 g tert. butylhydroperoxide were used in the
initiator feed, and 1.45 g ascorbic acid were used in
the catalyst feed.

20 The pressure sensitive adhesives of Examples 1-13
above were coated onto label quality monomerically
plasticized polyvinyl chloride facestock having a
thickness of 100 microns. The resultant pressure
sensitive adhesive films were tested for shear
adhesion, loop tack on glass and HDPE, peel adhesion,
percent shrinkage, removability and water resistance.
The coating weights and test results are shown in Table
25 1 below.

The shear adhesion test was performed according to
PSTC No. 7, except that the test area was 0.5 inch by
0.5 inch and the load was 500 g.

30 The loop tack/glass test was performed according to
Finat FTM 9. The loop tack/HDPE test was performed
according to Finat FTM 9 except that high density
polyethylene (HDPE) panels were used rather than glass.

35 The 90° peel/SS/20 M (minute) and 90° peel/SS/24 H
(hour) tests were performed according to Finat FTM 2
but on stainless steel rather than glass.

In the shrinkage test, a 10 x 10 cm sample of the
pressure sensitive adhesive film construction was

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1 applied to a glass plate and a cross was cut in the
middle in both directions. After a 20 minute dwell at
room temperature, the test plate with the sample was
aged at 70°C for 72 hours. The plate was then cooled
5 to room temperature and the distance between the two
halves of the tested film were measured and expressed
as a percentage of the original dimension, both in
machine and cross direction.

In the transfer or removability test, a 25 mm test
10 strip of the pressure sensitive adhesive film was
applied to a glass plate maintained at room temperature
for 20 minutes and then stored at 70°C for one week.
The plate was then cooled to room temperature and the
test strip manually removed. The plate was visually
15 observed for stain or residue.

The water resistance test was performed by placing
a drop of water onto the dried adhesive film in a work
area protected from draft. The area of the adhesive
underneath the water drop is observed for development
20 of haze or other discoloration for a period of 24
hours. The adhesives are ranked between "3+" or "+++"
and "3-" or "---" wherein the designations mean:

3+ = film remains clear for more than 30 min.
25 2+ = film remains clear (or develops a very slight
bluish haze) for at least 30 min.
1+ = film remains clear (or develops a very slight
bluish haze) for at least 5 min.
0 = film develops a slight bluish haze in less than
30 5 min.
1- = film develops a milky-white haze in 2 - 5 min.
2- = film develops a milky-white haze in less than
2 min.
3- = film turns completely white in less than 30
35 sec.

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1 WHAT IS CLAIMED IS:

1. A water-resistant acrylic emulsion pressure-sensitive adhesive comprising:

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a. from about 85% to about 97% by weight alkyl acrylate monomers;

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b. a positive amount up to about 3% by weight of polar monomers; and

c. a positive amount up to about 2% by weight of an external cross-linking agent.

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2. A pressure-sensitive adhesive as claimed in claim 1 further comprising up to about 2% by weight surfactant.

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3. A pressure-sensitive adhesive as claimed in claim 1 or 2 wherein the alkylacrylate is 2-ethylhexyl acrylate, butyl acrylate, heptyl acrylate, octyl acrylate, isooctyl acrylate, isobutyl acrylate, or a mixture thereof.

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4. A pressure-sensitive adhesive as claimed in any one of claims 1 to 3 wherein the polar monomer is methacrylic acid, acrylic acid, itaconic acid, maleic acid, acrylamide, methacrylamide 2-hydroxy ethyl acrylate, or mixtures thereof.

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1 5. A pressure-sensitive adhesive as claimed in any
one of the previous claims wherein an external cross-
linking agent is present and is of zirconium ammonium
5 carbonate, zinc ammonium carbonate, aluminum acetate,
zinc acetate, or mixtures thereof.

10 6. A pressure-sensitive adhesive as claimed in any
one of the previous claims in which there is present an
internal crosslinking agent in a positive amount up to
about one percent by weight.

15 7. A pressure-sensitive adhesive as claimed in
claim 6 wherein the internal crosslinking agent is of
polyethylene glycol diacrylate, hexanediol diacrylate,
20 ethoxylated trimethylolpropane triacrylate,
pentaerythritol triacrylate, propyleneglycol diacrylate,
diallyl maleate, diallyl phthalate, trimethylolpropane
trimethacrylate, or mixtures thereof.

25 8. A pressure-sensitive adhesive as claimed in any
one of the previous claims wherein up to about 15% of
the alkylacrylate is replaced by a hard monomer.

30 9. A pressure-sensitive adhesive as claimed in
claim 8 wherein the hard monomer is vinyl acetate,
styrene, methyl methacrylate, vinyl pyrrolidone, or
35 mixtures thereof.

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1 10. A pressure-sensitive adhesive as claimed in
claim any one of the previous claims in which the
adhesive is formed by emulsion polymerization in the
5 presence of a redox emulsion polymerization catalyst.

11. A pressure-sensitive adhesive as claimed in
claim 10 in which the redox emulsion polymerization
10 catalyst is a peroxide oxidase and a reductant which is
ascorbic acid or sodium formaldehyde sulfoxylate.

12. A pressure-sensitive adhesive as claimed in
15 claim 11 in which the peroxide is hydrogen peroxide or
hydroperoxides.

13. A water resistant, removable pressure-sensitive
20 adhesive as claimed in any one of the previous claims
in combination with a film face stock.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/00104

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : C08L 31/02, C09J 133/08

US CL : 524/556

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/556

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A, 4,507,429 (LENNEY) 26 March 1985 See Entire Reference.	1-3
X	US,A, 4,617,343 (WALKER ET AL) 14 October 1986 See Entire Reference.	1-3
X	US,A, 4,725,639 (LENNEY) 16 February 1988 See Entire Reference.	1-3
Y	US,A, 4,987,186 (AKIYAMA ET AL) 22 JANUARY 1991 See Entire Reference.	1-3



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be part of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

19 FEBRUARY 1993

Date of mailing of the international search report

26 APR 1993

Name and mailing address of the ISA/US
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US93/00104

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-13
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.